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MOISTURE DIFFUSION IN FIBER REINFORCED COMPOSITES.(U)
APR 78 J M WHITNEY
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MOISTURE DIFFUSION IN FIBER REINFORCED COMPOSITES

MECHANICS AND SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION

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PREFACE

In this report the mathematics of moisture diffusion as applied to laminated fiber reinforced composites are discussed.

The work reported here was performed in the Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. James M. Whitney of the Mechanics and Surface Interactions Branch was the principal investigator. The author wishes to thank W. Ragland of the University of Dayton Research Institute for the fabrication and testing of experimental specimens. This report was released by the author in February 1978, and covers the time period of August 1977 to January 1978.

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NOMENCLATURE

a	=	dimension of plate parallel to the x direction, in. (cm).
b	=	dimension of plate parallel to the y direction, in. (cm).
d_{ij}	=	elements of anisotropic diffusivity matrix, in^2/hr (mm^2/sec).
d_L	=	diffusivity parallel to the fibers in a unidirectional composite, in^2/hr (mm^2/sec).
d_R	=	diffusivity of resin, in^2/hr (mm^2/sec).
d_T	=	diffusivity normal to the fibers in a unidirectional composite, in^2/hr (mm^2/sec).
F_x, F_y, F_z	=	rate of transfer parallel to the x, y, and z axis, respectively of diffusing substance through a unit area of cross-section, % weight gain/hr/in ² (% weight gain/sec/mm ³).
h	=	plate thickness, in. (cm).
M	=	% weight gain
M_e	=	% weight gain at equilibrium
m	=	% weight gain/in ³ (% weight gain/mm ³).
m_e	=	% weight gain/in ³ (% weight gain/mm ³) at equilibrium.
T	=	temperature, °F (°C).
t	=	time, hr(sec).
V_f	=	fiber volume fraction, %.
θ	=	angle of fiber axis relative to the x axis in a unidirectional composite, radians.

SECTION I

INTRODUCTION

Moisture absorption in the presence of a humid environment is a basic physical property associated with current epoxy resins utilized in high performance composite materials. Such absorption causes plasticization of the resin to occur with concurrent swelling and lowering of the resin's glass transition temperature (temperature at which the polymer changes from a glassy solid to a rubbery solid). Because of the lowering of the resin glass transition temperature, there is considerable interest in determining the mechanical properties of composite laminates at various temperatures in the presence of moisture. Such experimental evaluation requires a knowledge of the moisture diffusion process in order to perform accelerated moisture conditioning and to determine moisture content and distribution during elevated temperature tests.

The mathematics of diffusion as applied to laminated composites is summarized in the present report. Theoretical results are compared to experimental data for graphite-epoxy composites, and some anomalies associated with laminates are discussed.

SECTION II

DIFFUSION IN A LAMINA

Consider an off-axis unidirectional lamina as shown in Figure 1. For the x-y axis system parallel to the sides, the diffusion equation takes the form (Reference 1)

$$m_{,t} + F_{x,x} + F_{y,y} + F_{z,z} = 0 \quad (1)$$

where a comma denotes partial differentiation. The rate of transfer of diffusing substance is related to the concentration gradient through Fick's law for an anisotropic media, which takes the form (Reference 1)

$$\begin{bmatrix} F_x \\ F_y \\ F_z \end{bmatrix} = \begin{bmatrix} d_{11} & d_{12} & 0 \\ d_{12} & d_{22} & 0 \\ 0 & 0 & d_{33} \end{bmatrix} \begin{bmatrix} -m_{,x} \\ -m_{,y} \\ -m_{,z} \end{bmatrix} \quad (2)$$

Substituting equation (2) into equation (1), assuming the diffusivities are constant, yields the results

$$m_{,t} = d_{11} m_{,xx} + 2d_{12} m_{,xy} + d_{22} m_{,yy} + d_{33} m_{,zz} \quad (3)$$

For the case of a unidirectional material containing square or hexagonal fiber packing

$$d_{33} = d_T$$

The in-plane diffusion coefficients in equation (2) can be expressed in terms of the diffusivities parallel and transverse to the fibers through the transformation relationships (Reference 1)

$$\begin{aligned} d_{11} &= d_L \cos^2 \theta + d_T \sin^2 \theta \\ d_{12} &= (d_T - d_L) \cos \theta \sin \theta \\ d_{22} &= d_L \sin^2 \theta + d_T \cos^2 \theta \end{aligned} \quad (4)$$

SECTION III

MICROMECHANICS OF DIFFUSION

Approximate micromechanics expressions for d_L and d_T have been derived by Springer and Tsai (Reference 2). For many advanced composites of interest, moisture absorption occurs only in the polymeric matrix material with the result (Reference 2)

$$d_L = (1 - V_f)d_R \quad (5)$$

$$d_T = (1 - 2\sqrt{V_f/\pi})d_R \quad (6)$$

Combining equations (5) and (6) yields

$$d_L = \left(\frac{1 - V_f}{1 - 2\sqrt{V_f/\pi}} \right) d_T \quad (7)$$

SECTION IV

DIFFUSION IN A LAMINATE

Since laminates are constructed of plies having fiber orientations in various directions, the diffusivity in any one direction will vary through the thickness. A solution for a laminate would require the solution of equation (3) ply-by-ply. A simplified approach can be developed by using "effective" constant diffusivities in conjunction with equation (3) which account for differences in diffusivities for individual plies. This approach is analogous to the development of laminated plate theory.

1. EFFECTIVE DIFFUSIVITY THROUGH-THE-THICKNESS

Consider a laminated slab subjected to one dimensional diffusion through-the-thickness, i.e.

$$m = m(z) \quad (8)$$

with the surface conditions

$$m(-h/2) = m_1, \quad m(h/2) = m_2 \quad (9)$$

where m_1 and m_2 are constants. For steady state, equation (1) reduces to

$$F_{z,z} = 0 \quad (10)$$

Integration of equation (10) yields

$$F_z = k_1 = \text{constant} \quad (11)$$

Equation (2) in conjunction with equations (8) and (11) yield

$$F_x = F_y = 0 \quad (12)$$

$$k_1 = -d_{33}(z) m_{,z}(z) \quad (13)$$

Separation of variables in equation (13), followed by integration through-the-thickness, and application of the surface conditions, equation (9), leads to the relationship

$$k_1 D = m_1 - m_2 \quad (14)$$

where

$$D = \int_{-h/2}^{h/2} \frac{dz}{d_{33}(z)} \quad (15)$$

Effective diffusivity, denoted by a bar, is defined by the relationship

$$F_z = \bar{d}_{33} m_{,z}(z) \quad (16)$$

Integration of equation (16) in conjunction with equations (9) and (11) yields

$$\frac{k_1 h}{\bar{d}_{33}} = m_1 - m_2 \quad (17)$$

Combining equations (14) and (17) yields

$$\bar{d}_{33} = \frac{h}{D} \quad (18)$$

For a laminate of N layers equation (15) takes the form

$$D = \sum_{i=1}^N \frac{h^i}{d_{33}^i} \quad (19)$$

where the superscript i denotes properties of the ith layer.

2. INPLANE EFFECTIVE DIFFUSIVITIES

Consider a laminated plate of thickness h having infinite length in the y direction and subjected to the surface conditions

$$m(x, \pm h/2) = m_1 + (m_2 - m_1) \frac{x}{a}, \quad (20)$$

$$m(0, z) = m_1, \quad m(a, z) = m_2 \quad (21)$$

Due to the variation of the diffusivities with respect to z , the problem is two dimensional in nature. A cursory examination of equations (1) and (2) reveals, however, that the steady state solution which satisfies the boundary conditions, equations (20) and (21), is the surface function defined by equation (21). Substituting equation (21) into equation (2) yields

$$F_x = d_{11}(z) \frac{(m_2 - m_1)}{a} \quad (22)$$

$$F_y = d_{12}(z) \frac{(m_2 - m_1)}{a} \quad (23)$$

$$F_z = 0 \quad (24)$$

Integrating equations (22) and (23) with respect to z and dividing by the thickness, h , yields

$$\frac{1}{h} \int_{-h/2}^{h/2} F_x dz = \bar{d}_{11} \frac{(m_2 - m_1)}{a} \quad (25)$$

$$\frac{1}{h} \int_{-h/2}^{h/2} F_y dz = \bar{d}_{12} \frac{(m_2 - m_1)}{a} \quad (26)$$

where the effective diffusivities, \bar{d}_{11} and \bar{d}_{12} are defined by the relationship

$$(\bar{d}_{11}, \bar{d}_{12}) = \frac{1}{h} \int_{-h/2}^{h/2} (d_{11}, d_{12}) dz \quad (27)$$

A similar problem with the finite dimension in the y direction yields

$$\bar{d}_{22} = \frac{1}{h} \int_{-h/2}^{h/2} d_{22} dz \quad (28)$$

Thus for a laminate of N layers the effective inplane diffusivities are simply an average through-the-thickness, i.e.

$$(\bar{d}_{11}, \bar{d}_{12}, \bar{d}_{22}) = \frac{1}{h} \sum_{i=1}^N (d_{11}^i, d_{12}^i, d_{22}^i) h^i \quad (29)$$

SECTION V

SOLUTION FOR A LAMINATED PLATE

(25) In most practical applications, fiber reinforced composite laminates are constructed of equal numbers of plies at $\pm\theta$. A cursory examination of equation (4) shows that

$$d_{12}(+\theta) = -d_{12}(-\theta) \quad (30)$$

Equation (30) in conjunction with equation (29) for an equal number of $\pm\theta$ plies yields

$$\bar{d}_{12} = 0 \quad (31)$$

Thus for most practical laminates, the governing equation for diffusion is of the form

$$m_{,t} = \bar{d}_{11}m_{,xx} + \bar{d}_{22}m_{,yy} + \bar{d}_{33}m_{,zz} \quad (32)$$

Consider a rectangular laminated plate containing an initial uniform moisture content, m_0 , with the origin of the coordinate system at the center of the plate, and subjected to a constant temperature and humidity condition, as described by the following initial and boundary conditions

$$m = m_0, \quad t \leq 0 \quad (33)$$

$$m(\pm a/2, y, z) = m(x, \pm b/2, z) \quad (34)$$

$$= m(x, y, \pm h/2) = m_e$$

A solution to equation (32) which satisfies the conditions of equations (33) and (34), is of the form (Reference 4)

$$m = m_0 + (m_e - m_0)g \quad (35)$$

where

$$g = 1 - m_1(x_1, t)m_2(x_2, t)m_3(x_3, t) \quad (36)$$

and $m_i(x_i, t)$ are solutions to the one dimensional equation

$$m_{i,t} = \bar{d}_{ii} m_{,x_i x_i}, \quad i = 1, 2, 3 \quad (37)$$

subjected to the conditions

$$m_i(x_i, t) = 1 \quad t \leq 1 \quad (38)$$

$$m_i(\pm a_i/2, t) = 0, \quad t > 0 \quad (39)$$

where x_1, x_2, x_3 , and a_1, a_2, a_3 correspond to x, y, z , and a, b, h , respectively.

Integration of equation (34) over the plate volume yields

$$M = M_0 + (M_e - M_0)G \quad (40)$$

where

$$G = 1 - M_1(t)M_2(t)M_3(t) \quad (41)$$

and

$$M_i(t) = \int_{-a_i/2}^{a_i/2} m_i(x_i, t) dx_i \quad (42)$$

1. TRIGONOMETRICAL-SERIES SOLUTION

A solution to equation (37) which satisfies the conditions of equations (38) and (39) can be obtained by classical separation of variables with the result (Reference 1)

$$m_i = \frac{4}{\pi} \sum_{k=0}^{\infty} \frac{(-1)^k}{(2k+1)} \cos(2k+1) \frac{\pi x_i}{a_i} \times \exp [-(2k+1)^2 \pi^2 t_i^*] \quad (43)$$

where

$$t_i^* = \frac{\bar{d}_{ii} t}{a_i^2} \quad (44)$$

Integration of equation (43) over the plate volume yields

$$M_i = \frac{8}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} \exp [-(2k+1)^2 \pi^2 t_i^*] \quad (45)$$

2. LAPLACE TRANSFORM SOLUTION

Short time solutions for either total weight gain or moisture distribution are often of practical interest. Because of the slow convergence of equations (43) and (45), an alternate solution to equations (37), (38), and (39) which provides rapid convergence for short times is desirable. Such a solution can be obtained from the Laplace transform method with the result (See Appendix)

$$m_i = 1 - \sum_{k=1}^{\infty} (-1)^{k+1} \left[\operatorname{erfc} \left(\frac{2k-1-2x_i/a_i}{4\sqrt{t_i^*}} \right) + \operatorname{erfc} \left(\frac{2k-1+2x_i/a_i}{4\sqrt{t_i^*}} \right) \right] \quad (46)$$

Integration of equation (46) yields

$$M_i = 1 - 4\sqrt{\frac{t_i^*}{\pi}} \left[1 + 2\sqrt{\pi} \sum_{k=1}^{\infty} (-1)^k \times \operatorname{ierfc} \frac{k}{2\sqrt{t_i^*}} \right] \quad (47)$$

3. APPROXIMATE SOLUTION

It has been noted by Weitsman (Reference 3) that for $t_i^* < 0.01$, equation (46) can be accurately represented by retaining only the first term. For

$t_i^* < 1$, the first three terms are sufficient for an accurate answer. Thus, the three-dimensional solution can be accurately approximated by the equations

$$g = 1 - \operatorname{erf} \left(\frac{1-2x/a}{4\sqrt{R_1 t^*}} \right) \operatorname{erf} \left(\frac{1-2y/b}{4\sqrt{R_2 t^*}} \right) \times \operatorname{erf} \left(\frac{1-2z/h}{4\sqrt{t^*}} \right), \quad t^* < 0.01 \quad (48)$$

$$g = 1 - \operatorname{erf} \left(\frac{1-2x/a}{4\sqrt{R_1 t^*}} \right) \operatorname{erf} \left(\frac{1-2y/b}{4\sqrt{R_2 t^*}} \right) \times \left\{ 1 - \sum_{k=1}^3 (-1)^{k+1} \left[\operatorname{erfc} \left(\frac{2k-1-2z/h}{4\sqrt{t^*}} \right) + \operatorname{erfc} \left(\frac{2k-1+2z/h}{4\sqrt{t^*}} \right) \right] \right\}, \quad 0.01 \leq t^* < 1 \quad (49)$$

$$g = 1, \quad 1 \leq t^* \quad (50)$$

where

$$R_1 = \frac{h^2 \bar{d}_{11}}{a^2 \bar{d}_{33}}, \quad R_2 = \frac{h^2 \bar{d}_{22}}{b^2 \bar{d}_{33}}, \quad t^* = \frac{\bar{d}_{33} t}{h^2} \quad (51)$$

Equations (48) and (49) utilize the identity

$$1 - \operatorname{erfc} u = \operatorname{erf} u \quad (52)$$

Equations (49), (50), and (51) are valid for $R_1, R_2 < 0.02$.

For $t_i^* < 0.07$, equation (47) can be adequately represented by the first term of the series (Reference 1). Similarly, a cursory examination of equation (45) reveals that for $t_i^* \geq 0.07$, the first term is adequate. Thus, for $R_1, R_2 < 0.1$,

$$G = 1 - \left(1 - 4\sqrt{\frac{R_1 t^*}{\pi}}\right) \left(1 - 4\sqrt{\frac{R_2 t^*}{\pi}}\right) \left(1 - 4\sqrt{\frac{t^*}{\pi}}\right), \quad (53)$$

$t^* < 0.07$

$$G = 1 - \frac{8}{\pi^2} \left(1 - 4\sqrt{\frac{R_1 t^*}{\pi}}\right) \left(1 - 4\sqrt{\frac{R_2 t^*}{\pi}}\right) \times \exp(-\pi^2 t^*), \quad 0.07 \leq t^* < 1 \quad (54)$$

$$G = 1, \quad t^* > 1 \quad (55)$$

4. SHORT TIME SOLUTION

Equation (53) in expanded form yields a third order polynomial in \sqrt{t} . For $R_1, R_2 < 0.1$ and $t^* < 0.01$, only the first order term need be retained with the result

$$G = 4\sqrt{\frac{\bar{d} t^*}{\pi}} \quad (56)$$

where

$$\frac{\bar{d}}{t^*} = \frac{d\bar{d}}{dt} \quad (57)$$

and \bar{d} is an effective diffusivity defined by the relationship

$$\bar{d} = \bar{d}_{33}(1 + \sqrt{R_1} + \sqrt{R_2})^2 \quad (58)$$

Thus a plot of G versus \sqrt{t} yields a straight line over the initial portion of the curve. The slope of the linear region is directly related to \bar{d} , i.e.

$$\bar{d} = \frac{\pi^2}{16} \left(\frac{G}{\sqrt{t}} \right)^2 \quad (59)$$

Equation (59) provides a relationship for experimentally determining \bar{d} .

5. ONE DIMENSIONAL APPROXIMATION

For the case where $R_1, R_2 < 0.002$, equation (56) can be used in conjunction with a one dimensional solution for total weight gain to predict an approximate three dimensional total weight with the result that equations (52), (53), and (54) become

$$G = 4\sqrt{\frac{\bar{t}^*}{\pi}}, \quad \bar{t}^* < 0.07 \quad (60)$$

$$G = 1 - \frac{8}{\pi^2} \exp(-\pi^2 \bar{t}^*), \quad 0.07 \leq \bar{t}^* < 1 \quad (61)$$

$$G = 1 \quad \bar{t}^* \geq 1 \quad (62)$$

This approximation was first suggested by Shen and Springer (Reference 6).

Note that for $\bar{t}^* = 0.07$, equations (60) and (61) yield a value of $G = 0.6$. Thus, the total weight gain will be a linear function of $\sqrt{\bar{t}^*}$ up to approximately 60% of equilibrium.

SECTION VI

NUMERICAL RESULTS

Consider a laminate constructed from plies of the same unidirectional material having symmetric fiber packing. As a result $\bar{d}_{33} = d_T$. For simplicity, consider laminate stacking geometries which yield $\bar{d}_{11} = \bar{d}_{22}$. A cursory examination of the transformations given in equation (4) shows the inplane diffusion coefficients to be independent of θ for this case. Thus, the laminate is quasi-isotropic with respect to the inplane diffusivities. Integration of equation (4) over all possible values of θ yields the following results for quasi-isotropic diffusion

$$\bar{d}_{11} = \bar{d}_{22} = \frac{d_L + d_T}{2} \quad (63)$$

Using equation (7) in conjunction with equation (63) yields

$$\bar{d}_{11} = \bar{d}_{22} = \frac{1 - \sqrt{V_f/\pi} - V_f/2}{1 - 2\sqrt{V_f/\pi}} d_T \quad (64)$$

The volume fraction is chosen as 0.6 for the present report. Actual volume fractions for graphite/epoxy laminates vary from about 0.6 to 0.65. Equation (64) now yields the result

$$\bar{d}_{11}/d_T = \bar{d}_{22}/d_T = 2.09 \quad (65)$$

In Figure 2 the moisture profile for two dimensional diffusion is shown across the centerline of a quasi-isotropic laminate for two values of t^* . Numerical results for total weight gain, along with experimental data, is shown in Figure 3 for a unidirectional graphite/epoxy composite and in Figures 4 and 5 for graphite/epoxy laminates having different thicknesses. Equations (7), (51), (54) and (65) were used in conjunction with specimen dimensions to generate the theoretical curves.

SECTION VII

EXPERIMENTAL DATA

In order to assess the accuracy of Fick's law, composite plates were fabricated from Hercule's AS/3501-5 graphite/epoxy pre-preg system, cut into small specimens, and exposed to equilibrium under various temperature and humidity conditions. One panel was a four ply unidirectional from which 2 in. (5cm) x 2 in. (5cm) specimens were cut. Two laminate panels were also fabricated. One panel was a four ply (0, 90)_s construction from which 2 in. (5cm) x 2 in. (5cm) specimens were cut. The second panel was constructed of twenty plies with the stacking geometry (0, 90)_{5s} from which 1 in. (2.54cm) x 1 in. (2.54cm) specimens were cut. Humidity exposures included underwater, UW, 95%, and 75%. Temperatures included 100°F (38°C), 120°F (49°C), 140°F (60°C), 160°F (71°C). Exposure procedures were in accordance with those described in Reference 5.

For the absorption data, percent weight gain was recorded for various exposure times. A value of M_e was determined by denoting an apparent equilibrium moisture content from the data. The weight gain values were an average of at least three specimens.

Values of M/M_e for the unidirectional composite specimens were tabulated as a function of \sqrt{t} for each exposure temperature. A linear regression analysis was used to fit the data over the range $0 \leq M/M_e \leq 0.6$, since R_1 , $R_2 < 0.002$ for the dimensions of the unidirectional specimens. The slope of this line was then used in conjunction with equation (59) to determine \bar{d} . For absorption from an initially dry condition, $M_0 = 0$, equation (40) reduces to $G = M/M_e$.

Equation (58) in conjunction with equations (7) and (51) yields

$$d_T = \frac{\bar{d}}{\left[1 + \frac{h}{a} \left(1 + \sqrt{\frac{1 - V_f}{1 - 2\sqrt{V_f/\pi}}} \right) \right]^2} \quad (65)$$

SECTION VIII

DISCUSSION

The importance of accelerated environmental conditioning techniques is illustrated in Figure 2. In particular, the severe changes in moisture gradient near the edge with respect to t^* are independent of material diffusion properties, but the rate of change of these gradients depends on the diffusion rates. Thus, high temperature moisture conditioning which produces large diffusion coefficients may induce edge cracks because of the rapid change in the moisture gradient at the edge.

A comparison of the data with Fick's law is illustrated in Figures 3-5. A cursory examination of equations (53) and (54) reveals that G is determined directly by the value of t^* if R_1 and R_2 remain constant. Thus, a plot of M/M_e versus $\sqrt{t^*}$ allows data from different relative humidities and temperatures to be plotted on one master plot.

Good correlation between data and theory is obtained for the unidirectional composite and thick bidirectional laminate while the correlation for the thin bidirectional laminate is only fair. A linear regression analysis of the data in Figure 4 yields a good fit to the theory for small values of t^* with the resulting values of d_T being considerably larger than those listed in Table 1 for the unidirectional composite. This procedure, however, leads to a poor fit for large values of t^* . This anomaly has been discussed in Reference 5 with respect to a possible cracking phenomenon or stress dependent diffusion process associated with large residual stresses which are present in bidirectional laminates. The fact that the same anomaly does not appear to occur in the thick laminate makes the precise mechanism more difficult to determine.

Experimentally determined values of d_T are shown in Table 1 as a function of temperature.

Table 1
EXPERIMENTALLY MEASURED DIFFUSIVITIES

T	$d_T(\text{IN}^2/\text{HR})$	$d_T(\text{MM}^2/\text{SEC})$
100°F(38°C)	5.65×10^{-7}	1.01×10^{-7}
120°F(49°C)	8.21×10^{-7}	1.47×10^{-7}
160°F(71°C)	2.02×10^{-6}	3.62×10^{-7}
180°F(82°C)	3.91×10^{-6}	7.00×10^{-7}

These values of d_T were used in conjunction with experimentally measured exposure times to establish values of t^* corresponding to the measured weight gains for the bidirectional laminates.

SECTION IX

CONCLUDING REMARKS

The mathematics of diffusion in a laminated composite can be described by simplified closed form expressions for the case of constant temperature and constant humidity exposure. These models assume the diffusion process to be independent of concentration. Comparison to data gives some confidence in the mathematical models. Anomalies associated with thin bidirectional laminates need to be resolved. Stress/strain effects on the diffusion process, time dependent material property changes, and cracks due to swelling are items which need further investigation. The micromechanics of diffusion, equations (5)-(7), do not recognize the interface as a possible source of diffusion. A more precise definition of the mechanisms associated with diffusion behavior are necessary before modified or advanced mathematical models of the diffusion process can be developed at either the micromechanical or macro-mechanical level.

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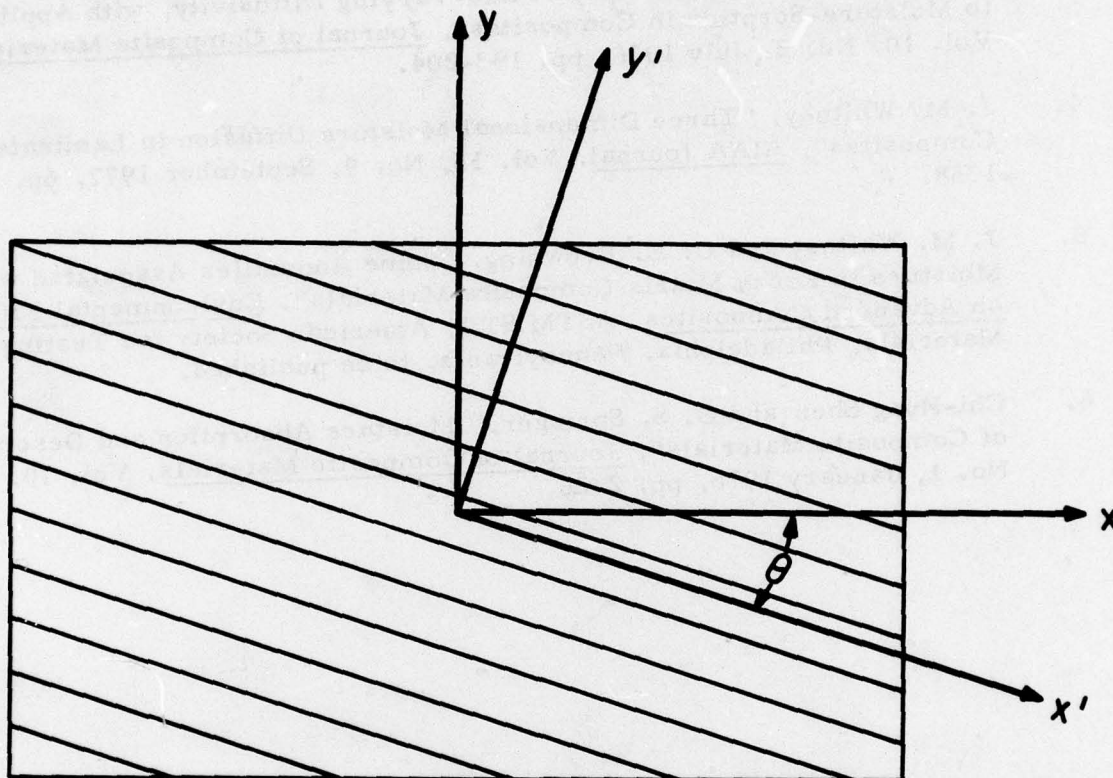


Figure 1. Off-Axis Unidirectional Lamina

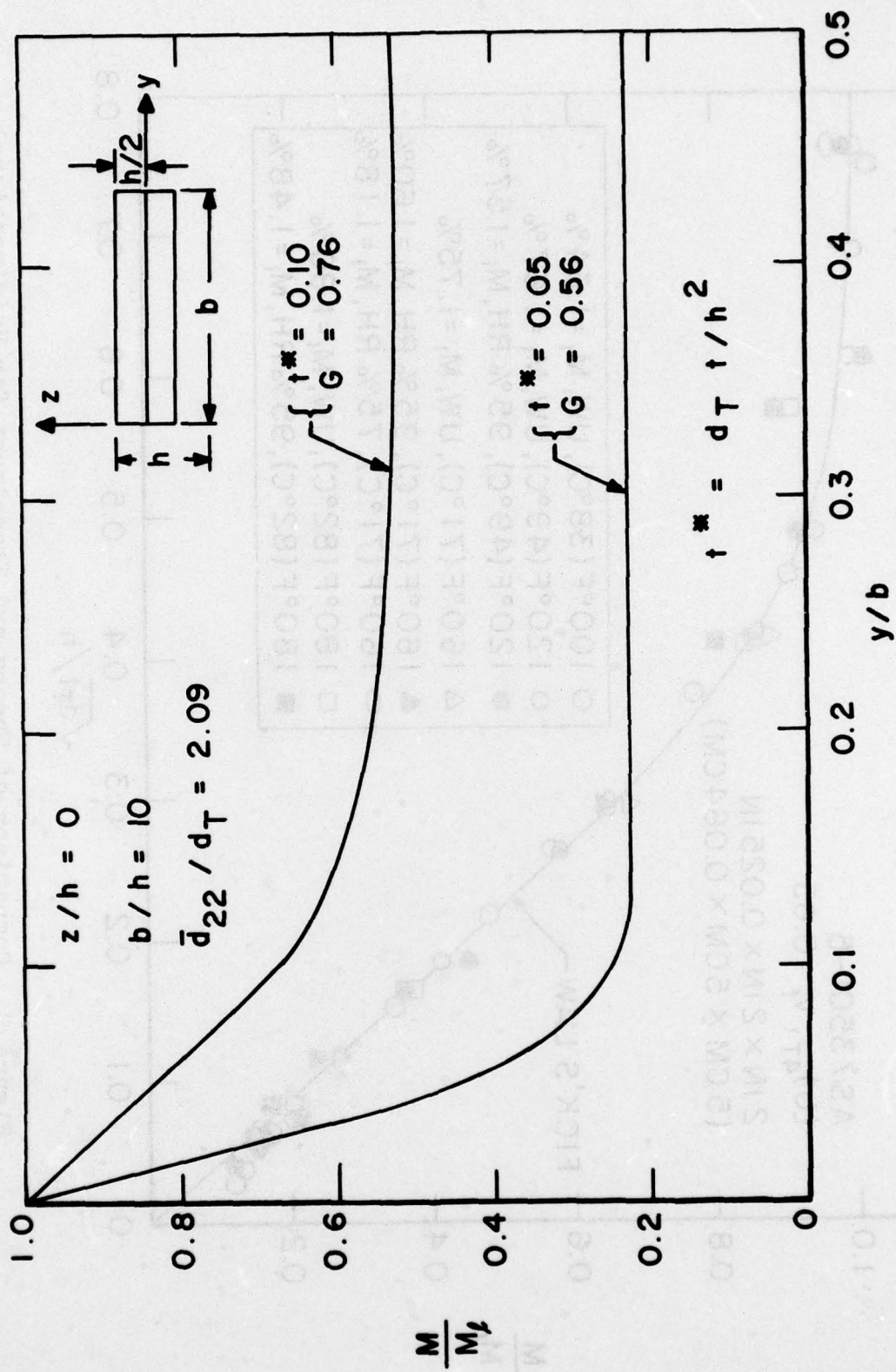


Figure 2. Moisture Profile Across Centerline of a Composite Laminate Subjected to Two Dimensional Diffusion

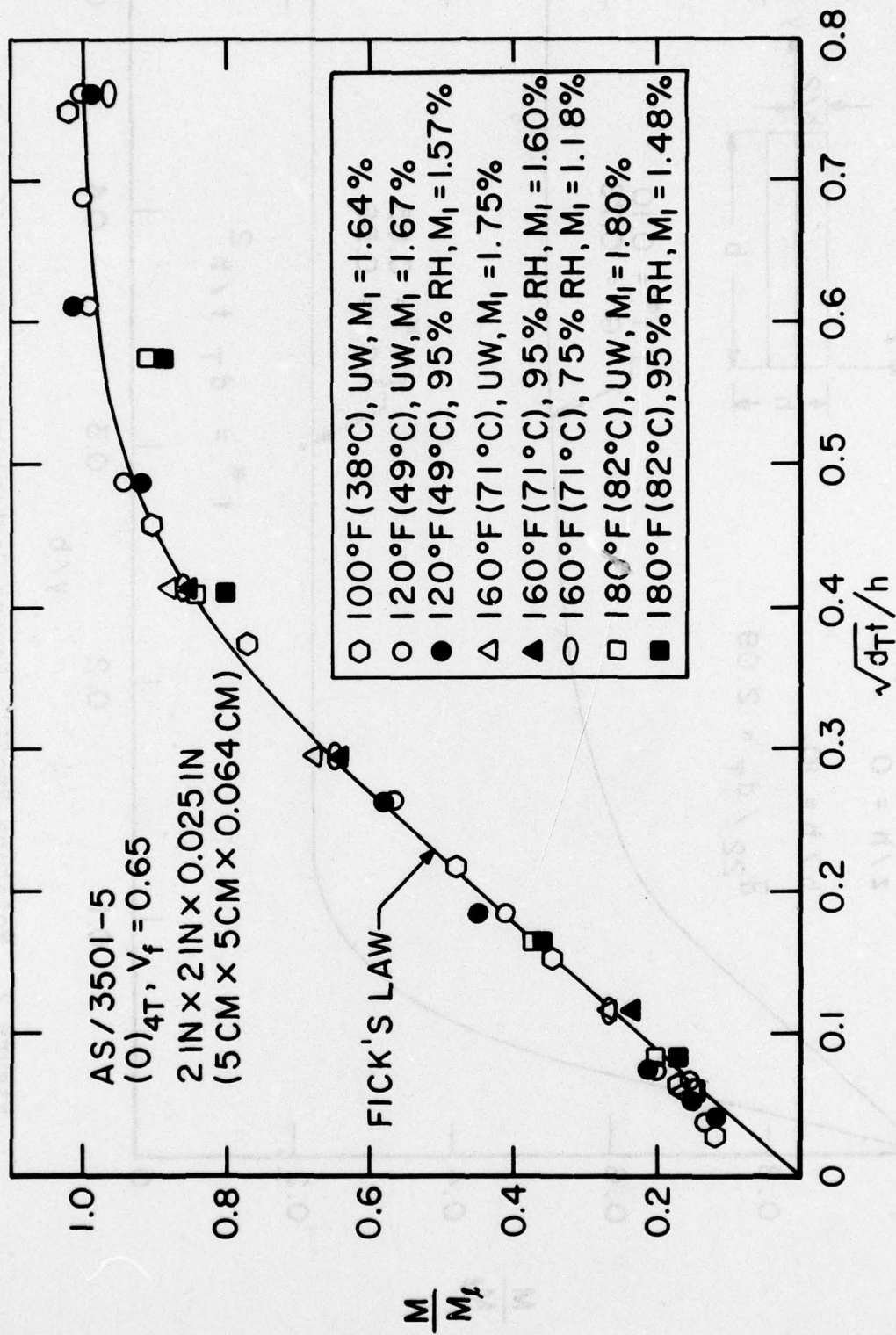


Figure 3. Comparison of Theory and Experiment for Unidirectional Composite

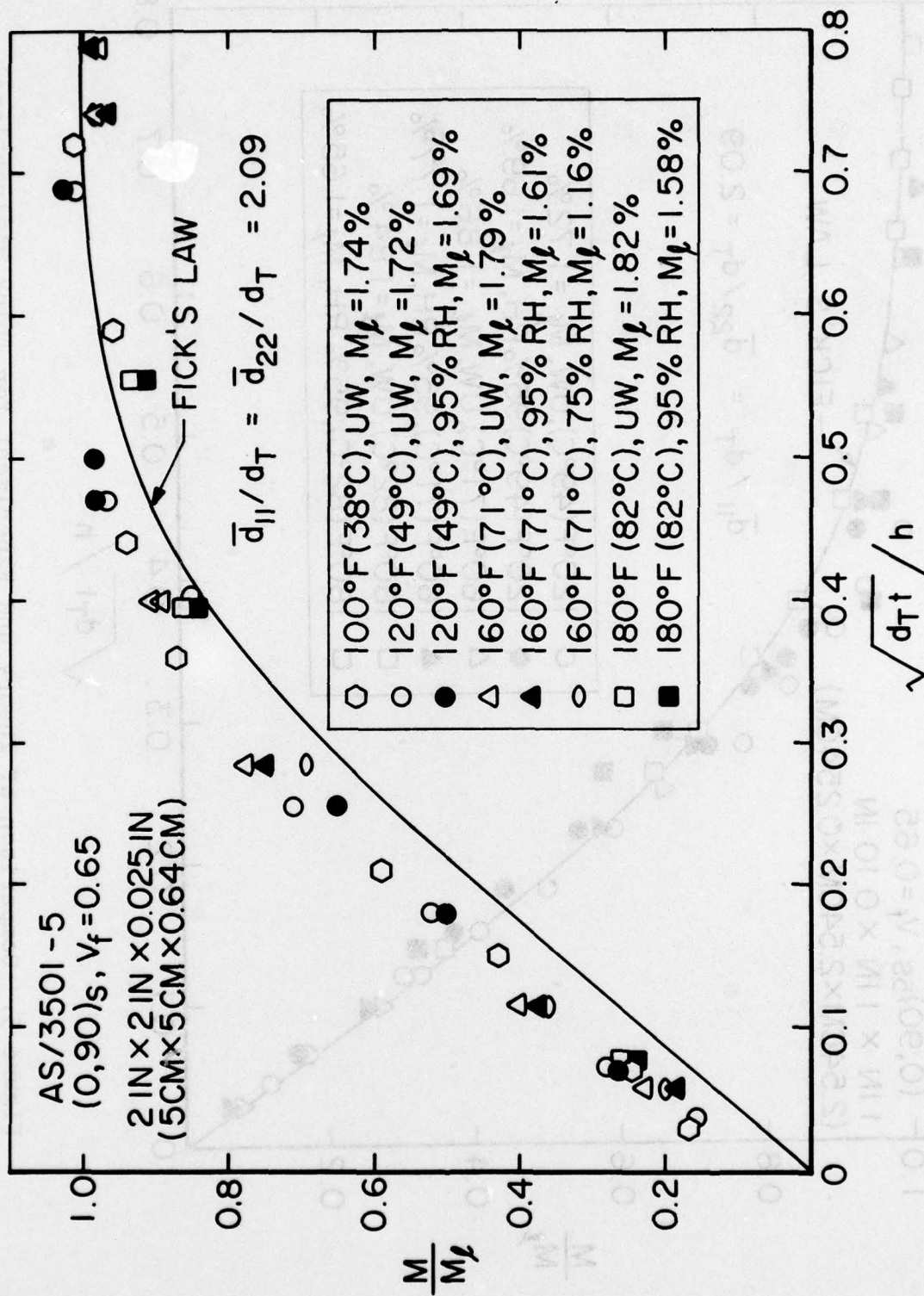


Figure 4. Comparison of Theory and Experiment for Thin Bidirectional Laminate

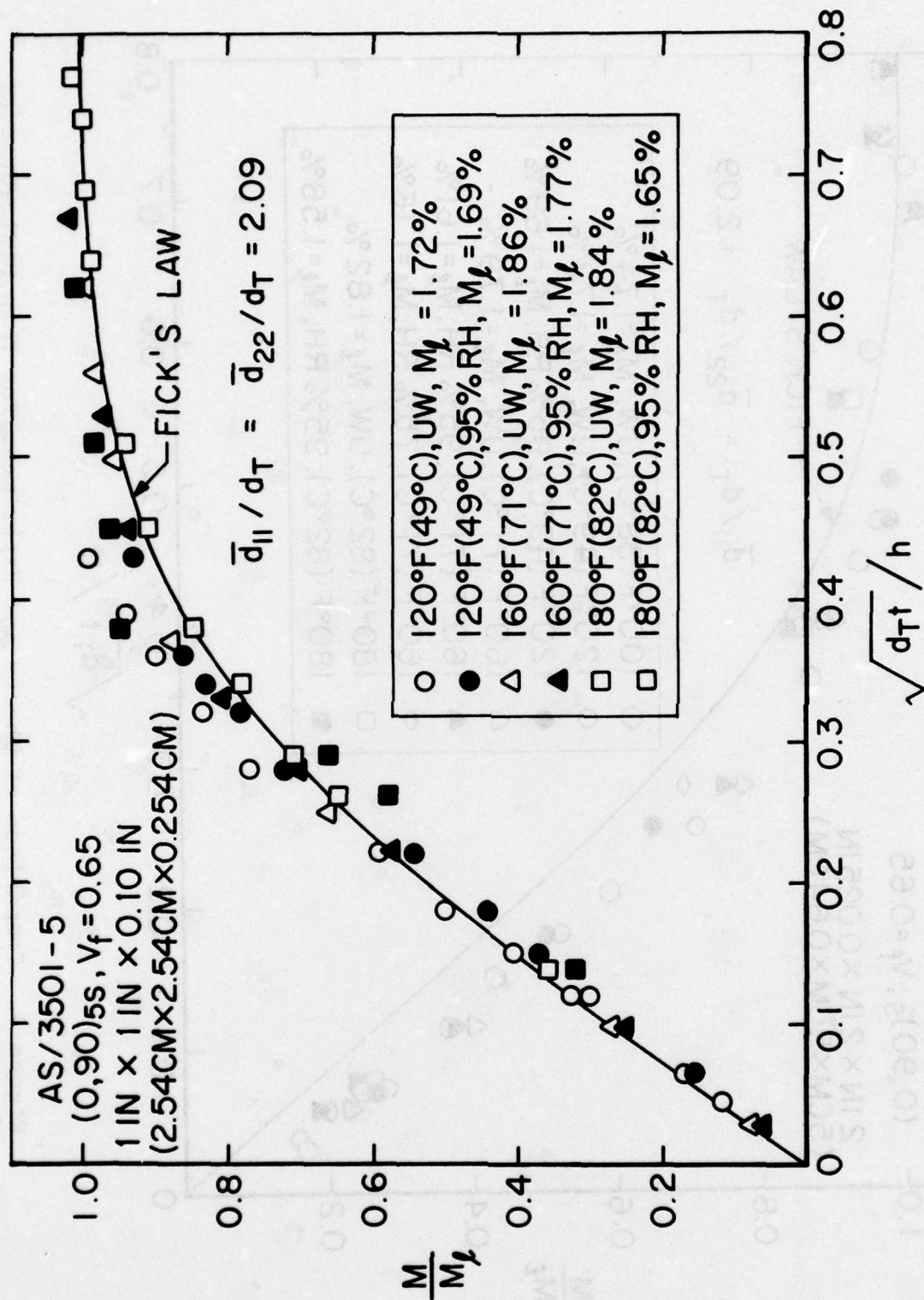


Figure 5. Comparison of Theory and Experiment for Thick Bidirectional Laminate